CLAIMS

Ç

1. A film-forming method of forming a titanium nitride film on a substrate to be processed through reaction of titanium tetrachloride and ammonia, said method comprising:

a first step of reacting titanium tetrachloride and ammonia with each other in supply-limited region, thereby forming a first titanium nitride layer on the substrate; and

a second step of reacting titanium tetrachloride and ammonia with each other in reaction-limited region, thereby forming a second titanium nitride layer on the first titanium nitride layer.

- 2. The film-forming method according to claim 1, wherein partial pressure ratio of the titanium tetrachloride to the ammonia in the first step is higher than that in the second step.
- 3. The film-forming method according to claim 2, wherein the partial pressure ratio of the titanium tetrachloride to the ammonia in the first step is not less than 0.13 but less than 0.2, and the partial pressure ratio of the titanium tetrachloride to the ammonia in the second step is not less than 0.2 but less than 1.5.
- 4. The film-forming method according to any one of claims 1 to 3, wherein temperature of the substrate in the first step is lower than that in the second step.
- 5. The film-forming method according to claim 5, wherein the temperature of the substrate in the first step is lower than 400°C, and the temperature of the substrate in the second step is not lower than 400°C.
- 6. A film-forming method of forming a titanium nitride film on a substrate to be processed in a chamber through reaction of titanium tetrachloride and ammonia, said method comprising:

3

a first step of supplying titanium tetrachloride and ammonia into the chamber with flow rate ratio of the titanium tetrachloride to the ammonia being a first flow rate ratio, while pressure in the chamber being maintained within a range of 3.94×10^{-4} to 1.32×10^{-2} atm, thereby forming a first titanium nitride layer on the substrate;

a second step of supplying titanium tetrachloride and ammonia into the chamber with flow rate ratio of the titanium tetrachloride to the ammonia being a second flow rate ratio smaller than the first flow rate ratio, while pressure in the chamber being maintained within a range of 3.94×10^{-4} to 1.32×10^{-2} atm, thereby forming a second titanium nitride layer on the first titanium nitride layer.

- 7. The film-forming method according to claim 6, wherein the first flow rate ratio is not less than 2.5 but not more than 60.
- 8. The film-forming method according to claim 6, wherein the first flow rate ratio is not less than 2.5 but not more than 15.
- 9. The film-forming method according to claim 6, wherein the first flow rate ratio is not less than 16, and the second flow rate is less than 16.
- 10. The film-forming method according to claim 9, wherein the second flow rate ratio is not less than 0.3 but not more than 10.
- 11. The film-forming method according to any one of claims 1 to 10, wherein the first and second titanium nitride layers are formed while the substrate is placed in the chamber in the first and second steps,

said method further comprising a step of purging an interior of the chamber with a purge gas after at least one of

the first and second steps.

~

- 12. The film-forming method according to claim 11, wherein the purge gas comprises at least one of nitrogen gas, hydrogen gas and argon gas.
- 13. The film-forming method according to any one of claims 1 to 12, further comprising a step of annealing at least one of the first titanium nitride layer and the second titanium nitride layer with a gas containing nitrogen atoms or hydrogen atoms after at least one of the first and second steps.
- 14. The film-forming method according to claim 13, wherein the gas containing nitrogen atoms or hydrogen atoms contains at least one of ammonia gas, hydrogen gas, nitrogen gas and monomethyl hydrazine gas.
- 15. A semiconductor device including the titanium nitride film formed by the film-forming method according to any one of claims 1 to 14.
- 16. A storage medium storing a software executable by a control computer of a film-forming apparatus, wherein upon execution of the software the control computer controls the film-forming apparatus so that the apparatus performs a film-forming method of forming a titanium nitride film, said method comprising:
- a first step of reacting titanium tetrachloride and ammonia with each other in supply-limited region, thereby forming a first titanium nitride layer on the substrate; and
- a second step of reacting titanium tetrachloride and ammonia with each other in reaction-limited region, thereby forming a second titanium nitride layer on the first titanium nitride layer.
- 17. A storage medium storing a software executable by a

Ç

control computer of a film-forming apparatus, wherein upon execution of the software the control computer controls the film-forming apparatus so that the apparatus performs a film-forming method of forming a titanium nitride film, said method comprising:

a first step of supplying titanium tetrachloride and ammonia into the chamber with flow rate ratio of the titanium tetrachloride to the ammonia being a first flow rate ratio, while pressure in the chamber being maintained within a range of 3.94×10^{-4} to 1.32×10^{-2} atm, thereby forming a first titanium nitride layer on the substrate;

a second step of supplying titanium tetrachloride and ammonia into the chamber with flow rate ratio of the titanium tetrachloride to the ammonia being a second flow rate ratio smaller than the first flow rate ratio, while pressure in the chamber being maintained within a range of 3.94×10^{-4} to 1.32×10^{-2} atm, thereby forming a second titanium nitride layer on the first titanium nitride layer.

18. A film-forming system for forming a titanium nitride film on a substrate through reaction of titanium tetrachloride and ammonia, said system comprising:

at least one film-forming apparatus including: a film-forming chamber; a substrate support member that supports a substrate in the film-forming chamber; a first supply line, provided thereon with a first gas flow controller, that supplies titanium tetrachloride into the film-forming chamber; a second supply line, provided thereon with a second gas flow controller, that supplies titanium ammonia into the film-forming chamber; and an exhaust device that evacuates an atmosphere in the film-forming chamber; and

a control unit that controls said at least one of the film-forming apparatus so that the apparatus performs a first step of reacting titanium tetrachloride and ammonia with each other in supply-limited region, thereby forming a first titanium nitride layer on the substrate, and a second step of reacting

titanium tetrachloride and ammonia with each other in reaction-limited region, thereby forming a second titanium nitride layer on the first titanium nitride layer.